Lecture 16

Physics 404

We go back to the problem of an ideal gas. Consider the solutions to the Schrodinger equation for a single particle in a box, as we did before (Lecture 9). We call these solutions 'orbitals'. There are an infinite number of such solutions. We make the leap and assume that if there are N identical particles in the box, and they do not interact, we can describe the system as being occupied by N particles occupying N single-particle orbitals. This is a big assumption that will be revisited later.

The spin-statistics theorem of quantum mechanics states that there are two types of elementary particles: Fermions (of half-integer spin) and Bosons (of integer spin). A list of elementary particles and their spins is posted on the class web site.

If many identical Fermions are placed in a box and there is strong overlap of the wavefunctions, the Pauli exclusion principle says that no two of these Fermions can occupy the same exact quantum state. This places a strong constraint on the Gibbs sum for the Fermion case. These considerations do not apply to many identical Boson systems. In the Fermion case, a particular orbital can either be un-occupied or occupied by exactly 1 particle. In the Boson case, any number of particles can occupy a particular orbital, including 0.

First we will calculate the Gibbs sum for the Fermion case. We consider the system to be a single orbital, arbitrarily chosen from the infinite number of single-particle orbitals available to a particle in a box. The reservoir is the set of all other orbitals. We assume that the system and reservoir are in both thermal and diffusive equilibrium. The Gibbs sum is $\mathcal{Z} = \sum_{N=0} \quad \sum_{\varepsilon_s(N)} e^{(N\mu-\varepsilon_s)/\tau} = \sum_{N=0}^{1} \quad \sum_{\varepsilon_s(N)} e^{(N\mu-\varepsilon_s)/\tau} = e^{(0\mu-\varepsilon_{s(0)})/\tau} + e^{(1\mu-\varepsilon_{s(1)})/\tau}$. We adopt the convention that the zero particle state is the zero of energy $\varepsilon_{s(0)} = 0$. The single particle state has an energy we call $\varepsilon_{s(1)} = \varepsilon$. The Gibbs sum becomes $\mathcal{Z} = 1 + e^{(\mu-\varepsilon)/\tau} = 1 + \lambda e^{-\varepsilon/\tau}$, where λ is the activity. The thermal average occupancy of the state can be calculated simply as $\langle N \rangle = 0 \times \frac{1}{1+e^{(\mu-\varepsilon)/\tau}} + 1 \times \frac{\lambda e^{-\varepsilon/\tau}}{1+e^{(\mu-\varepsilon)/\tau}} = \frac{\lambda e^{-\varepsilon/\tau}}{1+e^{(\mu-\varepsilon)/\tau}}$. Dividing top and bottom by $\lambda e^{-\varepsilon/\tau}$ gives $f(\varepsilon) = \langle N \rangle = \frac{1}{e^{(\varepsilon-\mu)/\tau}+1}$, which is known as the Fermi-Dirac distribution. We will make a further leap by saying that this distribution applies for any orbital of any energy ε, because the original choice of orbital was arbitrary. At zero temperature this distribution is $f(\varepsilon) = 1$, for $\varepsilon - \mu < 0$, and $f(\varepsilon) = 0$, for $\varepsilon - \mu > 0$. In other words all the states of energy below μ are filled, and all states above μ are empty. The filled states are sometimes called the 'Fermi sea'. At finite temperature, the discontinuous distribution softens with $f(\varepsilon = \mu) = 1/2$. Only Fermions within energies a few τ below μ will be 'promoted' to the un-occupied higher energy states above μ.

Next we derive the Gibbs sum for the Boson case. Once again we consider the system to be a single orbital, arbitrarily chosen from the infinite number of single-particle orbitals available to a particle in a box. The reservoir is the set of all other orbitals. We assume that the system and reservoir are in both thermal and diffusive equilibrium. The Gibbs sum is $\mathcal{Z} = \sum_{N=0} \quad \sum_{\varepsilon_s(N)} e^{(N\mu-\varepsilon_s)/\tau}$, and any number of particles can go into the orbital, hence the first sum could go up to N. For a large system, N is effectively infinite. The orbital has a single-particle energy of ε, and we assume that when it is occupied by N particles the energy of the system is simply $\varepsilon_s(N) = N\varepsilon$. The Gibbs sum now becomes

$\mathcal{Z} = \sum_{N=0}^{\infty} e^{(N\mu - N\varepsilon)/\tau} = \sum_{N=0}^{\infty} \left(\lambda e^{-\varepsilon/\tau}\right)^N$. If we assume that $\lambda e^{-\varepsilon/\tau} < 1$, then this sum will converge to $\mathcal{Z} = \frac{1}{1-\lambda e^{-\varepsilon/\tau}}$. We can evaluate the thermal average occupation number as $\langle N \rangle = \lambda \frac{\partial \log \mathcal{Z}}{\partial \lambda}$, which gives $f(\varepsilon) = \langle N \rangle = \frac{1}{\frac{1}{\lambda} e^{\varepsilon/\tau} - 1} = \frac{1}{e^{(\varepsilon-\mu)/\tau} - 1}$, which is known as the Bose-Einstein distribution. Note that it differs from the Fermi-Dirac distribution only in the minus sign in the denominator!

Taking the logarithm of both sides of the convergence condition $\lambda e^{-\varepsilon/\tau} < 1$ for Bosons results in the constraint $\frac{\varepsilon-\mu}{\tau} > 0$, which says that the chemical potential is bounded above by the lowest energy orbital in the system.

Note that in the limit $\frac{\varepsilon-\mu}{\tau} \gg 1$, both distributions go to the same functional form, $f(\varepsilon) \approx e^{-(\varepsilon-\mu)/\tau}$, which is the classical limit $f(\varepsilon) \ll 1$, which is equivalent to the dilute limit $\frac{n}{n_Q} \ll 1$.